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A study of a lead mining waste water pollution problem

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Department:

A STUDY OF A LEAD MINING WASTE WATER POLLUTION PROBLEM

BY

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THESIS

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ABSTRACT

The waste water from the Fletcher Mine of the St. Joseph Lead Company was producing large algal growths in Bee Fork Creek. A field and laboratory study was conducted to determine the characteristics of the waste, find a method of determining the pollutional materials contained in the waste, study the undesirable algal growths, and develop and evaluate a practical, inexpensive, and effective pollution abatement method. Laboratory studies included: analytical analysis of the waste, flotation reagent analysis, a microscopic study of the algal growths, algal growth studies, and heavy metal analysis of the algal growths. Field work comprised: a study of the mining and milling processes, evaluation of waste water samples, observation of the tailings ponds, collection of algal samples, and the evaluation of surface baffles in the tailings ponds.

The characterization of the waste indicated that some normal parameters for evaluating waste water are not applicable to mining waste. The flotation reagent analysis and algal growth studies were unsuccessful, but, the algal growths were found to be composed of the blue-green algae, Oscillatoria, and contained high concentrations of heavy metals. The surface baffles prevented the outflow of the surface film which improved the condition of Bee Fork Creek.

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I. INTRODUCTION

A. History

The lure of rich mineral deposits has been responsible for the exploration and settlement of much of the Western Hemisphere. Such is also true of the southeastern section of Missouri. Early settlers in Illinois learned from the Indians that lead could be found in the region west of the Mississippi River. In 1719, the French, who then owned the territory, organized the French Company of the West and sent an expedition to southeastern Missouri to set up mining operations. The expedition was led by Renualt and included 200 miners and laborers plus slaves.

Renualt's exploration parties discovered and mined lead deposits in various parts of what are now Washington, Madison, and St. Francois Counties, Missouri (1). This region has become known as the "Southeastern Missouri Lead Belt" (Figure 1). The largest early lead deposit discovery was Mine La Motte, discovered by La Motte in Madison County in 1720 and immediately brought into production.

Other lead deposits were discovered southeast of Potosi, Missouri along the Big River in St. Francois County during the early 1800's. The demand for lead during the Civil War raised its price and following the war, production continued to increase. The first metallic zinc was produced at Potosi in 1867 and by 1880, lead and zinc mining was a major industry in Missouri. Lead production

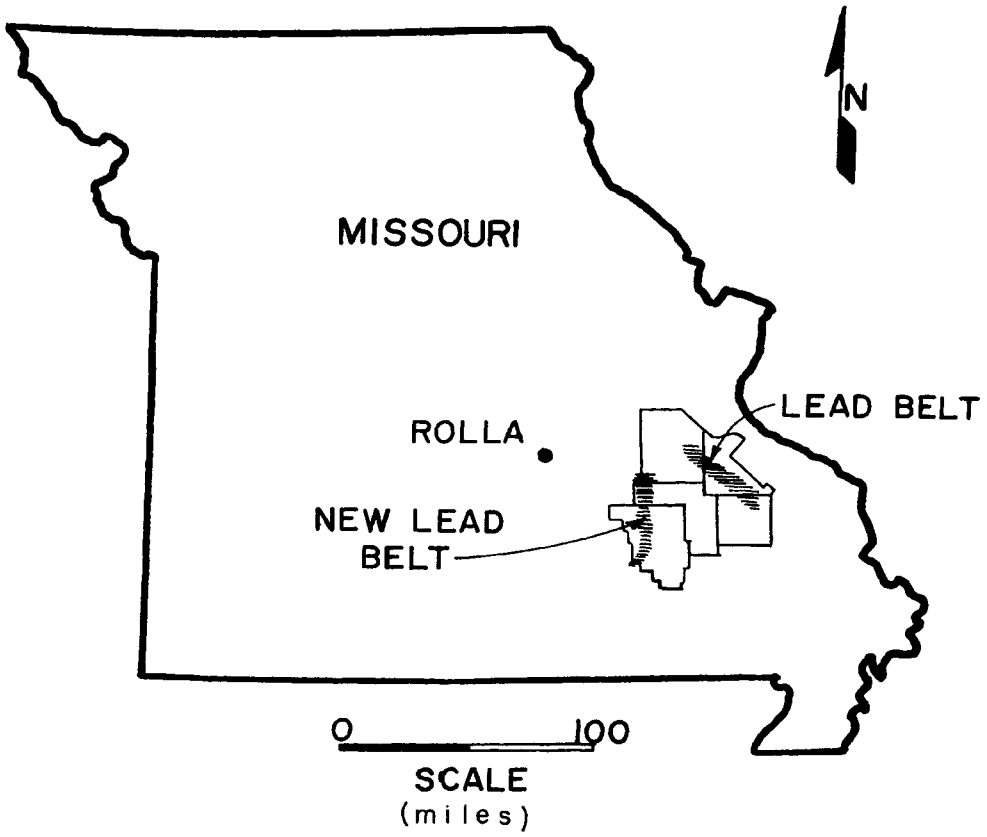

Figure 1. Location of the Lead Belt and New Lead Belt in Southeast Missouri

was at its peak during World I, World II, and the Korean War, however, zinc production dropped sharply after World War I (2).

The first major lead ore discovery in southeast Missouri outside of the established lead belt, was at the Indian Creek Mine in Washington County. The lead deposit was found in 1947 by diamond drilling 950 feet.

The discovery of lead ore near Viburnum in 1955 , by the St. Joseph Lead Co., climaxed twenty-six years of investigation of this area. In 1929, when the first magnetic survey of Missouri was being made, engineers reported erratic magnetometer readings in the area of Bourbon, Missouri. In 1943, the Missouri Geological Survey published a magnetic map of the State which was made by taking magnetic readings at one mile intervals along roads in the State. This map also recorded magnetic anomalies of considerable magnitude in the Bourbon area. Further geophysical investigations were conducted from 1946 to 1948 using improved airborne equipment to make aeromagnetic surveys. These surveys again showed unusual magnetic anomalies in the Bourbon area.

A cooperative exploratory program was then undertaken by the U. S. Government, the State of Missouri, and private industry to determine the cause of the unusual magnetic anomalies. The result of the program was the discovery of the Pea Ridge high grade iron ore deposit in 1955. However,

at about the same time, one of the exploratory holes drilled to the south of Pea Ridge in Crawford County struck high grade lead ore. This prompted further drilling in the area and by 1962, a new lead ore belt was found to extend over 36 miles almost due South from Viburnum, Missouri (2) (Figure 1). The name given to this find was the "Viburnum Trend" or "New Lead Belt".

Most of the lead ore was found to occur in the upper part of the Cambrian Bonneterre Formation, mostly dolomite, at depths ranging from 700 to 1,200 feet (2). Galena (lead sulfide) was found to be the principal ore mineral with lesser quantities of sphalerite (zinc sulfide) and chalcopyrite (copper-iron sulfide) (2).

The southeastern part of Missouri, which includes the New Lead Belt, has always had an abundant supply of water. With an annual precipitation of 44 inches and many creeks, springs, rivers, and shallow ground water tables, there has been little concern about water conservation in the area. However, with the rapid developement of the newly discovered mineral resources in the area, it became evident that the waste water from the mining and milling operations could have a detrimental effect on the beautiful clear water streams of the area.

B. Previous Work

A research project (3) was initiated in 1967 at the University of Missouri-Rolla to investigate the initial

shock and the following long term cumulative effects of the mining waste water on the water quality and biota of the affected streams. The results of the first year of study were reported by Wixson, et al., (4) and Handler (5). They found that considerable changes in water quality and stream ecology had taken place in Bee Fork Creek below the discharge of Fletcher Mine of the St. Joseph Lead Co. which could be directly or indirectly related to the mining operations. These changes were: an increase in turbidity, pH, alkalinity, hardness, fluoride, total dissolved solids, and heavy metals content of the water and a reduction in the population of fishes and benthic animals in a two-mile stretch of the stream immediately below the mine and mill tailings discharge; the development of an intense growth of algae and bacteria which completely covered the stream bottom immediately below the mine discharge.

The heavy metal concentrations had not reached levels which were toxic to fish, but the excessive algal growth did present a very serious problem (Figure 2). This thesis presents the results of a study of the Fletcher mining and milling waste water and the problems associated with it.

C. Objectives

The disposal of mining and milling waste waters of the Fletcher Mine of the St. Joseph Lead Company has

Figure 2. Undesirable Growths of Bacteria and Blue-Green Algae, Oscillatoria, in Bee Fork Creek.

altered the natural water quality of Bee Fork Creek and caused a prolific algal growth in the stream bottom. The objectives of this study were:

1. To determine the make-up and characteristics of the mining and milling waste waters.
2. To find a method of determining the polluting materials contained in the waste water.
3. To study the characteristics of the algal growths produced by the polluted waters.
4. To develop and evaluate a practical, inexpensive, and effective pollution abatement method.

D. Scope

In order to achieve the proposed objectives, both field and laboratory work were performed. The mine, mill, and tailings ponds of the Fletcher Plant of the St. Joseph Lead Company were utilized for the field site of the study. Field work was comprised of the following:

1. A study of the water usage in the mine and mill.
2. A study of the mining and milling processes used at the Fletcher Plant.
3. Evaluation of waste water samples from the mine and mill discharges.
4. Observation and study of the three tailings ponds which receive the mine and mill waste water.
5. Collection and study of the algal growths causing problems.

The studies and analyses performed on the laboratory involved the following:

1. An evaluation of physical and chemical characteristics of the waste water samples to determine BOD (biochemical oxygen demand), COD (chemical oxygen demand), total solids, phosphorus, nitrogen, and fluoride concentrations.
2. An analysis for sodium isopropyl xanthate by means of potentiometric titration.
3. A microscopic examination of undesirable algal growths.
4. Studies using algal growths from the field to determine the algal nutrient value of flotation process waste water.
5. Measurement of the concentrations of lead, zinc, and copper in the algal mats.

II. THE AREA OF STUDY

A. The Fletcher Plant

The Fletcher Plant is the newest and most modern lead mining operation of the St. Joseph Lead Company. The plant consists of the mine, ore concentrating mill, office and maintenance building, and the three tailings ponds which receive the shaft and mill waste waters (Figure 3). The location of the plant is near the intersections of Highways TT and KK in Reynolds County, Missouri. After four years of construction and a capital investment of 12.5 million dollars (6), the Fletcher Plant was put into production in February, 1967 (7). Because of the modern automated equipment installed at the Fletcher Plant, only about 140 men (8) are required to mine and concentrate some 5,000 tons of ore per day (7).

1. The Mine

The lead, zinc, and copper ore is mined on two levels; the upper level at an elevation of 980 feet and the lower level at an elevation of 1,116 feet (9). There are two vertical shafts to the mining levels. The smaller of the two shafts is seven feet in diameter and is utilized for ventilation and transporting men and materials to and from the mine. The larger shaft is twelve feet in diameter and is used for hoisting the ore, previously crushed in the mine, to the surface.

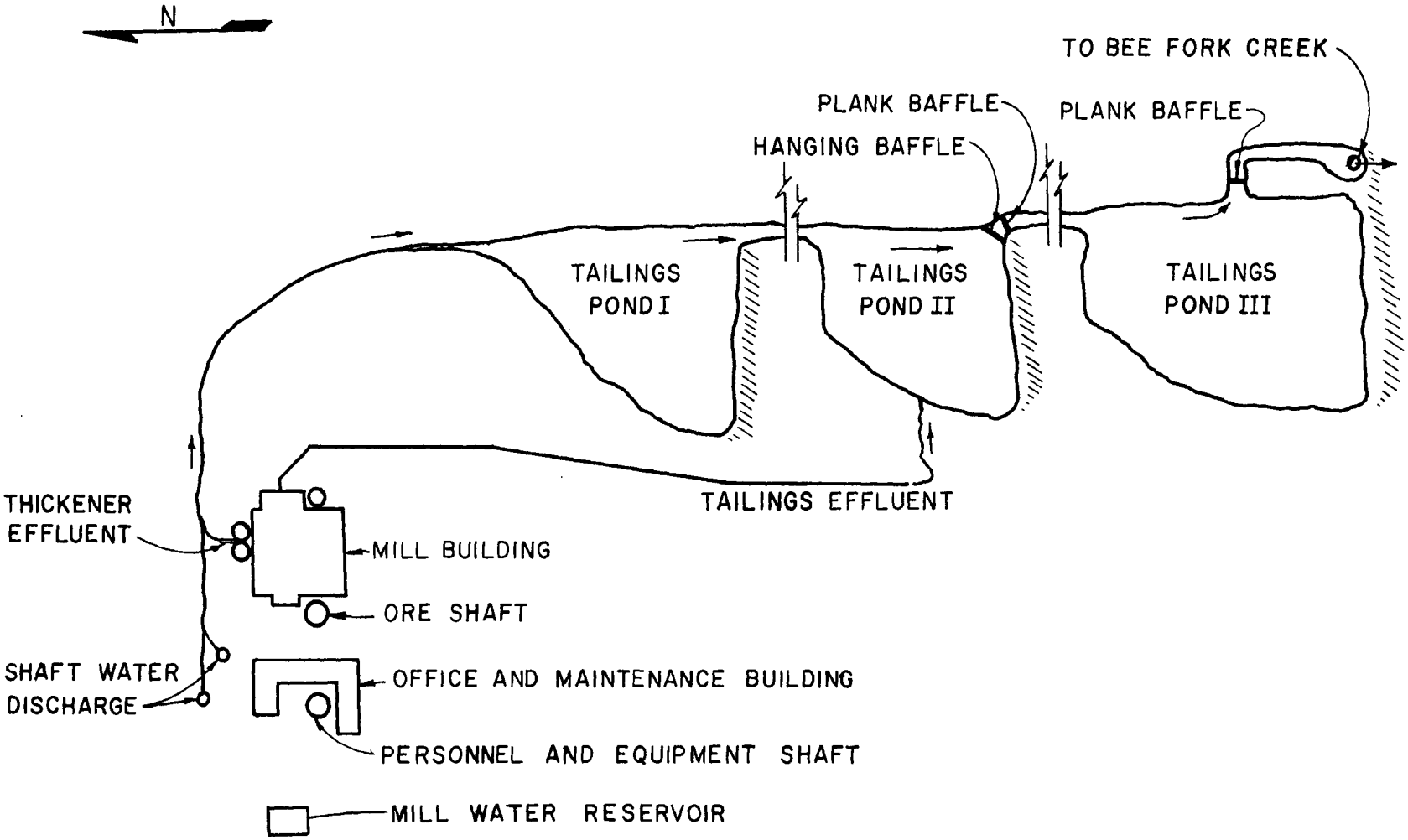

Figure 3. Schematic Diagram of the Fletcher Plant

The mining levels are located in the Bonneterre Formation, mostly a dolomite, which contains a great quantity of subsurface water. This subsurface water leaks into the mine at a rate of 5,000 to 5,500 gallons per minute (Figure 4) and must be pumped from the lower level to the surface (Figure 5). About 1,250 to 1,400 gpm of the shaft water is diverted to a reservoir and becomes the process water for the milling operation.

2. The Ore Concentrating Mill

The purpose of the ore concentrating mill is to separate the ore minerals from the rock, mostly dolomite, and prepare them for shipment to the smelter. The ore separation is accomplished by a process of selective mineral flotation. A schematic diagram of the process is shown in Figure 6.

The ore previously crushed in the mine, is mixed with water to form a slurry and then flotation reagents are added (Figure 7). The ore, after being further crushed in the rod mill, is segregated in a cyclone. The fine particles go directly to the lead flotation circuit and the coarse particles are crushed again in a ball mill (Figure 8).

In the lead flotation circuit, the ore slurry flows into the shallow tanks of the flotation machines. An air froth is introduced into the bottom of the flotation machine tanks where, with the aid of the flotation reagents

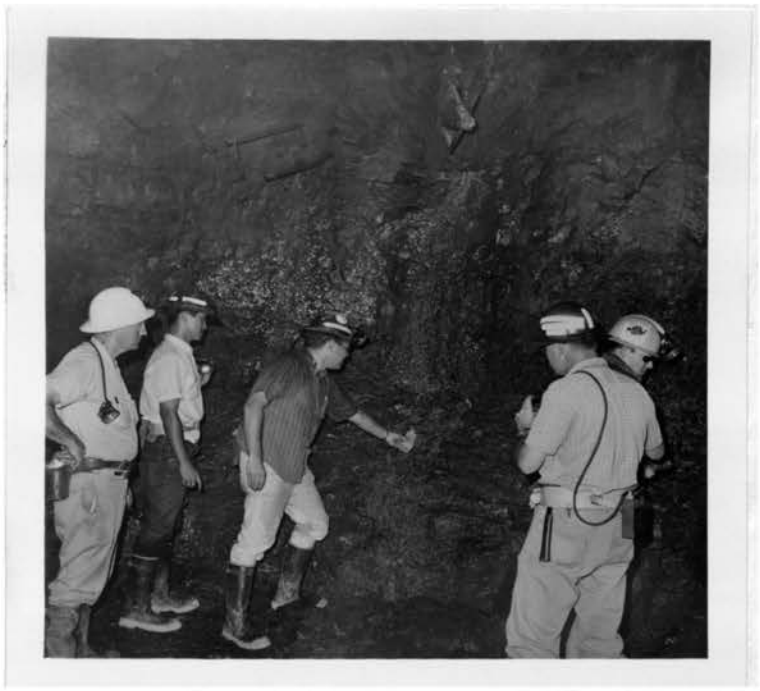

Figure 4. Subsurface Water Flowing into the Fletcher Mine.

Figure 5. One of Two 12-Inch Subsurface Shaft Water Discharge Pipes.

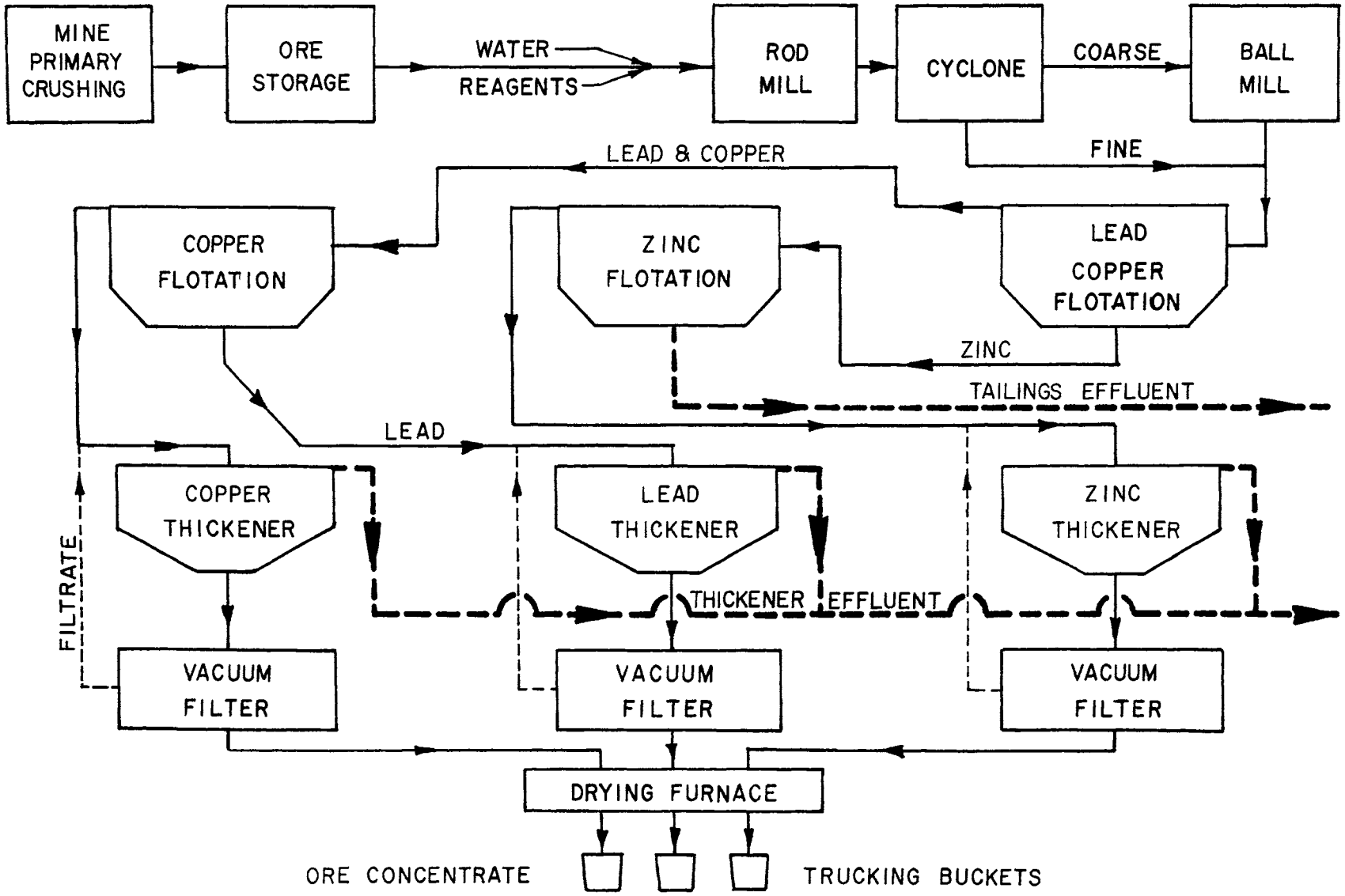

Figure 6. Schematic Diagram of the Ore Concentrating Process at the Fletcher Mill.

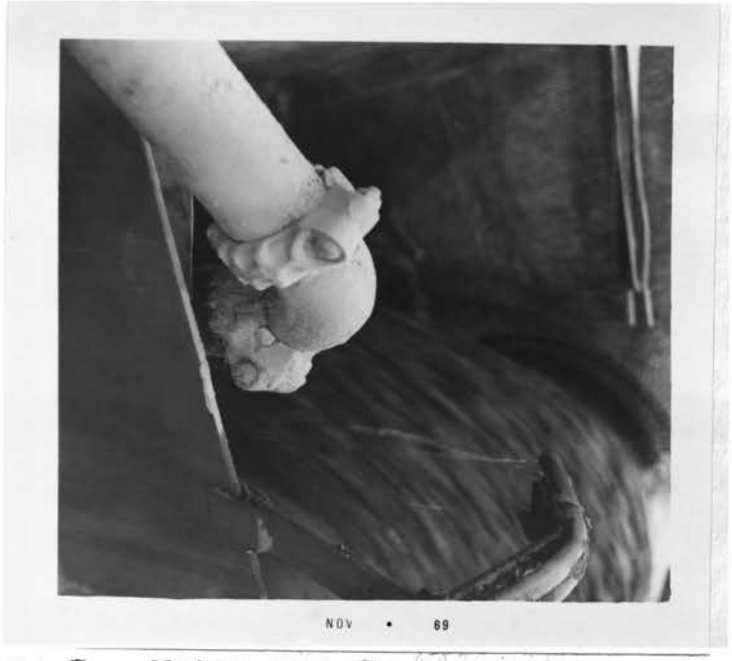

Figure 7. Water and Flotation Reagents Being Added to the Ore Before Going to the Ball Mill.

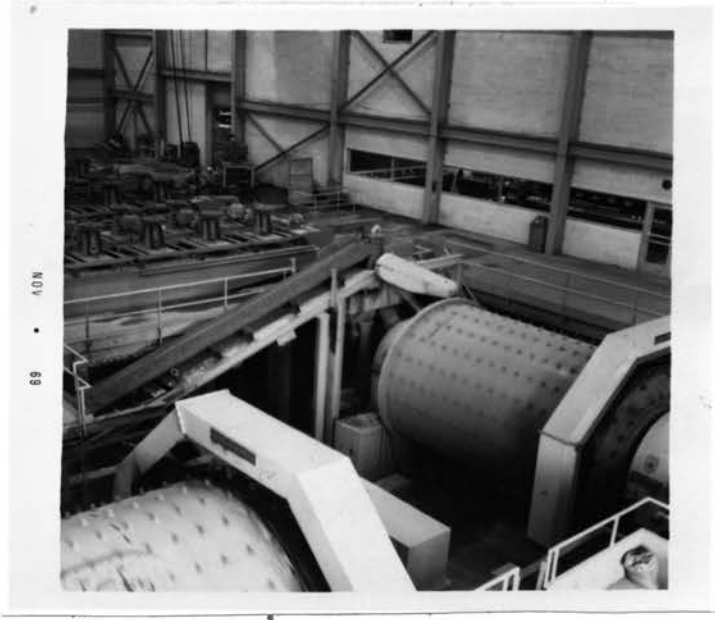

Figure 8. View of Ore Concentrating Mill Showing the Ball and Rod Mill in the Foreground and the Flotation Machines in the Background. Note Control Room in the Upper Right Hand Corner.

the lead and copper sulfide minerals are attached to the air bubbles and float to the water surface; the zinc sulfide minerals stay at the bottom of the tanks with the tailings (dolomite rock). The main types of flotation reagents are shown in Table I which includes: (1) collectors, such as sodium isopropyl xanthate; (2) frothers, which usually consist of pine oils or mixed alcohols; and (3) activating and drepressing agents (Table I). The collector coats only the sulfide minerals while the frother enables the water to form an air froth in which the individual air bubbles are coated with a thin film of the frother. The collector coated sulfide minerals are attracted to the frother coated air bubbles and thus, float together. The zinc does not float because of the zinc depressing agents added. A more detailed explanation of the flotation process has been presented by Gaudin (10).

Upon reaching the water surface, the froth containing lead and copper minerals spill over a weir into a launder (Figure 9) and are piped to the copper flotation circuit where reagents are added to float the copper and depress the lead, thus, separating the two minerals. The zinc minerals and the tailings are discharged from the bottom of the lead flotation tanks and pumped to the zinc flotation circuit where zinc flotation reagents are added to allow the zinc minerals to be floated. The discharge from the bottom of the zinc flotation tanks is the final tailings.

TABLE I

The Flotation Reagents Used at the Fletcher Mill

Reagent	Purpose
Sodium Isopropyl Xanthate	Collector
Isopropyl Ethyldithiocarbomate	Collector
Mixed Alcohols (6 to 9 carbons)	Frother
Zinc Sulfate ($ZnSO_4$)	Zinc Depressant
Sodium Cyanide (NaCN)	Zinc Depressant
Copper Sulfate ($CuSO_4 \cdot 5H_2O$)	Zinc Activant
Sodium Dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$)	Lead Depressant
Sulfur Dioxide (SO_2)	Lead Depressant
Starch	Lead Depressant

Figure 9. Froth Containing Lead and Copper Minerals Spilling Over the Weir of the Flotation Machines.

The feed rate of flotation reagents is controlled by a computer which receives information on the ore concentrations from an X-ray analyzer and adjusts the reagent feed rates accordingly.

The separated lead, zinc, and copper mineral concentrates are each piped to their own respective concentrate thickener tank (Figure 10). In the thickener, the concentrate settles to the bottom of the tank while the water and excess flotation reagent mixture flows out the top (Figure 11). This waste water is discharged directly into the shaft water stream, as shown in Figure 12, and flows to the tailings ponds. The thickened concentrate slurry is pumped from the bottom of the thickeners to vacuum filters where much of the remaining water is removed (Figure 13). The dried concentrate is then taken by a conveyor to a drying furnace where all of the remaining water is driven off and the concentrate is then loaded into buckets for trucking to the smelter.

3. The Tailings Ponds

The three tailings ponds are held back by dams built of earth, rock, and compacted tailings. The ponds are located in a long deep valley which slopes down from the mine and mill site. The three ponds are constructed in series.

The three sources of water which flow into the tailings ponds are the mine shaft water, the lead, zinc,

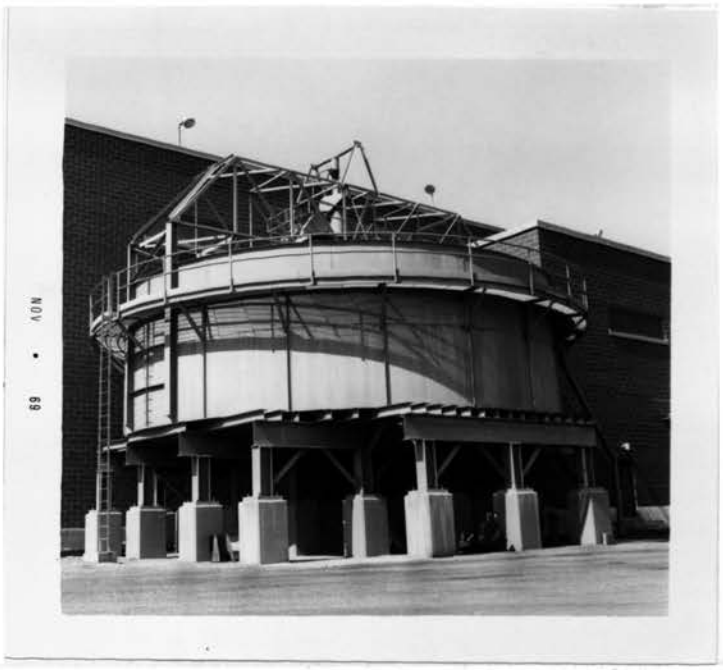

Figure 10. The Copper Concentrate Thickener.

Figure 11. Surface Weir of the Zinc Concentrate Thickener.

Figure 12. Lead and Zinc Thickener Effluent. Note Subsurface Shaft Water Discharged in Foreground.

Figure 13. Thickened Concentrate Being Vacuum Filtered.

and copper thickener effluents and the tailings effluent. The thickener effluents are mixed with the shaft water before flowing directly to the first tailings pond while the tailings effluent is usually pumped to the hill above the tailings ponds and used for road and dam construction (Figure 14). The excess water is drained from the tailings and flows into Tailings Pond II.

Since the ponds tend to fill up as the tailings are discharged into them, the dams are enlarged as required. The three ponds have a total hydraulic detention time of approximately 60 days. But, each pond has a surface spillway and there is evidence that the detention time of the surface flow is very much less than the hydraulic detention time. Thus, any floating pollutant such as waste reagents, scums, and oils, would be discharged with little detention from the spillway of Tailings Pond III (Figure 15) directly into Bee Fork Creek.

B. Bee Fork Creek

Bee Fork Creek, a tributary of the Black River, receives the mining and milling waste water directly from the effluent of the Fletcher Plant Tailings Pond III. From its source, one mile southeast of Bunker, Missouri (Figure 16), the creek flows eastwardly 16 miles in a sand and gravel bed until it flows into the West Fork of the Black River three miles above Centerville, Missouri. Bee Fork's drainage basin covers an area of about 35 square

Figure 14. Road Fill Constructed of Compacted Tailings.

Figure 15. Effluent Pipe, Tailings Pond III.

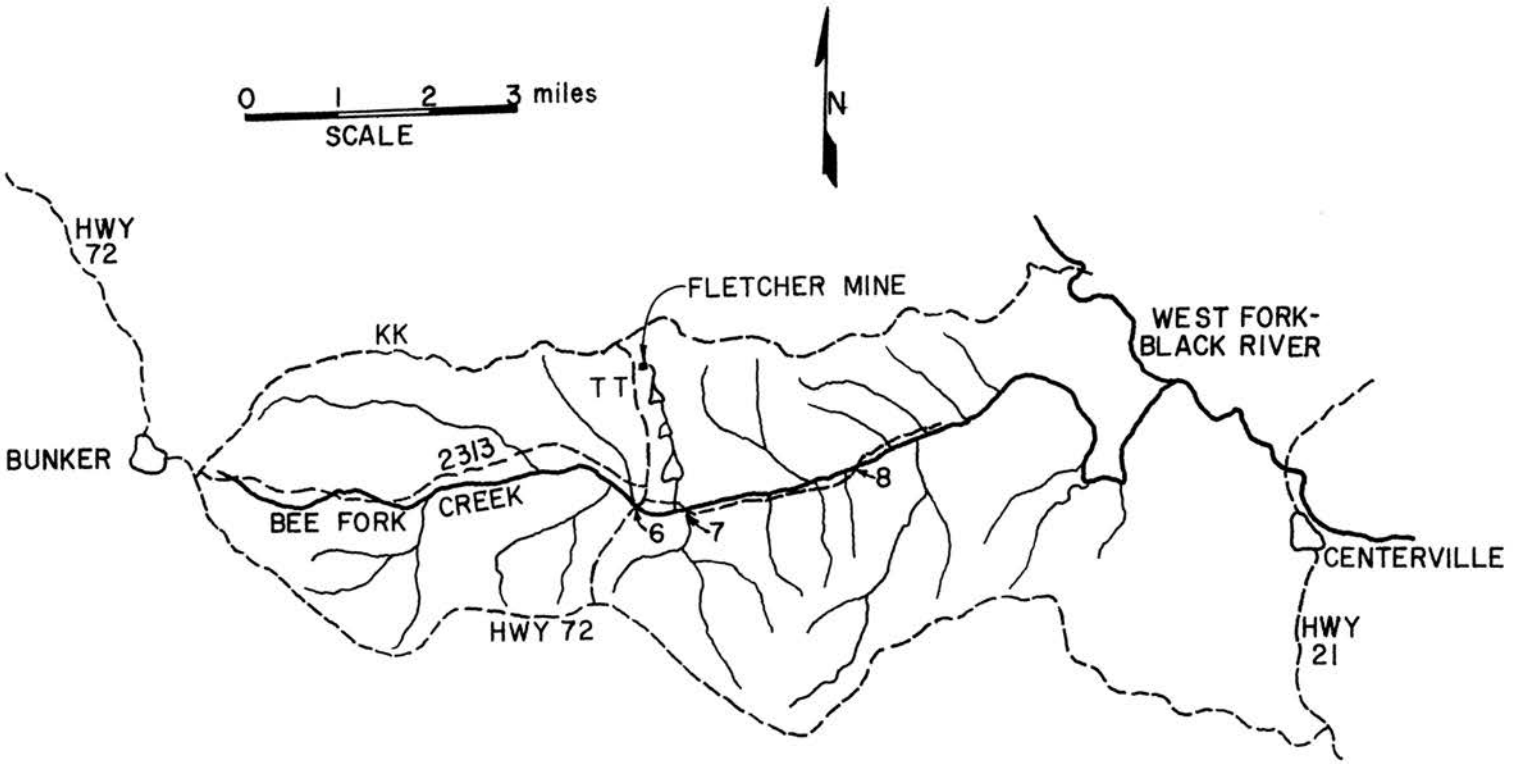

Figure 16. Location of the Sampling Stations on Bee Fork Creek.

miles, and its waters are normally very clean and support abundant aquatic life. The flow of the creek varies considerably with seasonal rain fall. Flow measurements at two points of the creek are presented in Table II.

Three water quality sampling stations, Station 6, Station 7, and Station 8, were established on Bee Fork Creek in 1968. The numbers assigned to these sampling stations were in accordance with an overall research project which included other streams of the area (4). The locations of these three stations are shown in Figure 16.

1. Station 6

Station 6 is located at the low water bridge on Reynolds County Highway TT, approximately two miles upstream from the Fletcher Plant effluent. Because the creek is not polluted at this point, Station 6 was selected as a control station.

2. Station 7

Station 7 is located at the low water bridge on Forest Road 2313, about one-half mile downstream from the Fletcher Plant effluent. At this point, the creek water and the Fletcher Plant waste water are well mixed, which was the reason for the selection of this site.

3. Station 8

Station 8 is located at the low water bridge on Forest Road 2313, approximately two and one-half miles down-

stream from the Fletcher Plant effluent. This point was selected so that the persistence of the pollution and stream recovery could be evaluated.

TABLE II

Flow Characteristics of Bee Fork Creek (11)

Location of Measurement	Date	Discharge cfs
NE¼ sec. 25, T.32N., R.2W, at low-water bridge on County Highway TT, 5 miles east of Bunker, Missouri	9-30-65 1-26-66 8-10-66 10-24-67	10.00 4.55 1.54 4.10
NW¼ sec. 30, T.32N., R.1W., 100 ft. upstream from low-water bridge on County Highway, 5½ miles east of Bunker, Missouri	9-30-65 1-26-66 8-10-66 10-24-67	11.50 5.62 2.66 14.40

III. REVIEW OF THE LITERATURE

A. Water Pollution by Mining Waste Reagents

When waste water from an ore flotation process leaves the mill, it usually is discharged into some receiving waters. Once the waste reagents reach an aquatic body such as ponds, streams, or rivers, the organic materials may be biologically decomposed causing various pollutional effects depending upon the characteristics of the waste reagents and the natural waters.

One of the earliest reports of water pollution by mining waste reagents was a study by Asmangulyan of the Vokchi River in 1959 (12). This study indicated that the river was considerably polluted by waste water from two ore beneficiating factories. Considerable xanthates, cresols, and other organic flotation reagents along with waste rock were found in the river water. The oxidizability of the waste waters from the ore beneficiating factories was reported to vary between 323 to 4,960 mg/l. A bacteriological study showed that the waste waters were sterile. This was attributed to the bacteriocidal substances used in the flotation processes. It was found that due to the swift current of the Vokchi River, chemical and bacteriological self-purification was completed at 24 kilometers down stream from the point of waste discharge.

In 1965, two Russian engineers, Pavlenko and Savelova (13), established the maximum permissible concentrations of

the two Russian flotation reagents, OPS-M and OPS-B, in bodies of water. From the results of the tests made on warm blooded animals, they concluded that the maximum allowable concentrations of OPS-M for hygienic-toxicological purposes was 0.5 mg/l and the maximum allowable concentration of OPS-B for sanitation purposes was 2 mg/l. The threshold odor concentrations of the reagents were 250 mg/l for OPS-M and 7 mg/l for OPS-B. They also reported that OPS-M did not affect the BOD kinetics or general sanitary conditions at the 250 mg/l concentration, but, OPS-B had a BOD of 2 mg/l at the 7 mg/l concentration.

In 1966, another Russian engineer, Voskoboinikova (14) reported that the maximum permissible concentration of another Russian flotation reagent, IM-68 was 0.03 mg/l. This value was based upon a five month long study on warm blooded animals for the toxic effects of IM-68 and the hexyl, heptyl, and octyl alcohols.

The effects of a lead, zinc, and copper flotation process waste water on Bee Fork Creek in southeast Missouri was reported by Wixson, et al., (4) and Handler (5) in 1969. The waste water exhibited little BOD but caused an increased growth of bacteria and produced large mats of the blue-green algae, Oscillatoria. The algal mats first appeared about one-half mile below the tailings pond discharge and continued down stream for several miles depending upon seasonal temperature variations.

B. Detection and Analysis of Flotation Reagents

One of the first methods for detecting xanthates was the spectrophotometric analysis proposed by Bushell and Malnarich in 1956 (15). A sample of potassium isopropyl xanthate was purified by dissolving in ethyl alcohol, filtering off the insoluble residue, and precipitating the filtrate with diethyl ether. The precipitate was then retreated by the same procedure and the purified xanthate was washed with ether and dried. The spectrum of a solution of the purified xanthate in water was determined. The peak, at 301 mu wavelength, provided a basis for quantitative analysis.

It was found that certain frothers interfered seriously with the xanthate analysis, so, the method cannot be used for solutions containing frothers.

Another method of flotation reagent analysis was proposed by Du Rietz in 1957 (16). Purified grades of xanthates and other flotation reagents were analyzed by potentiometric titration with silver nitrate ($AgNO_3$) solution. A silver electrode and a saturated calomel reference electrode were used to measure the potential of the solution. The xanthates were in the potential range from -460 to -220 mv. Other potentiometrically active substances, such as sulfides, had potentials below -48 mv and other reagents, such as thiosulfate, were found to

have potentials above -200 mv. This information formed the basis for practical xanthate analysis.

In 1960, Leonchenkova (17), developed a luminescent analysis for flotation waste. Organic and inorganic solvents were used to obtain solutions of the flotation reagents. The luminescent analysis was then made using a special apparatus consisting of an excitation source, two cuvettes (for samples and standard solutions), and a photometer. The luminescence of the flotation reagent waste was compared against that of a standard. The determination was said to be simple and highly accurate.

Another study of luminescent analysis was reported by Russian engineers in 1968 (18). The luminescence of 14 flotation reagents was determined by using a mercury quartz lamp as a luminescence source. This method was used for determining the resulting reagent concentrations after flotation. It was first necessary to determine the fluorescence intensity as a function of the reagent concentration and to check for the possibility of certain concentrations of the flotation reagents than had previously been possible.

A photocolorimetric determination of flotation reagents was developed by a Russian engineer, Onisiforova, in 1960 (19). He reported that the determination of cationic collectors in the presence of frothing agents can be made by measuring the absorbance of a colorimetric solution of the reagents.

The detection of flotation reagents by measuring the surface tension of the waste water was developed by a group of Russian engineers in 1968 (20). Standards were set up by measuring the surface tension of water containing various amounts of flotation reagents of different pH. The presence of the flotation reagents could be detected at concentrations as low as 0.02% using this method.

C. Flotation Reagent Waste Treatment Methods

A Russian report made in 1958 by Maslenitskii and Dolivo-Dobrovol'skii (21) pointed out after analysis of flotation process waste water, the necessity for discontinuing their direct discharge into surrounding bodies of water. The most ecconomical solution was to clarify the waste water and reuse the clarified water in the ore concentrating mills. Treatment with chlorinated lime or hypochlorite removes all ordinary flotation reagents except phenols, cresols, kerosine, and cresyl aerofloat. In some cases, it was better to use slaked lime or ferrous sulfate with slaked lime. The chemical consumption varied from 0.5 to 2.5 kg per cubic meter of flotation waste water treated.

In a study of the Tekeli Lead-Zinc Mill waste water (22), it was recommended that the mine shaft water and the flotation tailings and waste water be combined and discharged into the tailings pond. Also, the phenolic

fothing agents should be replaced with nonphenolic reagents because the flotation waste contained from 18 to 30 mg/l phenol. It was predicted that complete clarification of the mixed waste could be achieved in 6 to 8 hours with a residual suspended solids concentration of 5 to 10 mg/l.

The flotation mill waste from the Apuseni Mountain Plant in Romania (23) were discharged into a settling tank which drained into a river. Several analyses were conducted by Tararu to determine that toxic substances were present in the plant effluent. It was decided that further treatment was necessary. A larger settling tank with increased detention time and aeration added proved sufficient to break down the xanthate while sodium hypochlorite was added to eliminate the cycanide ion. These modifications removed the unwanted reagents from the flotation mill waste water.

IV. METHODS AND PROCEDURES

In order to achieve the proposed objectives, both field and laboratory work was performed. Field work included studies of the water usage in the plant and of the mining and milling processes used at Fletcher Mine. Waste water samples from the mine and mill discharges were evaluated. The three tailings ponds which receive the mining and milling waste water were observed and studied. Based on recommendations made during this study, surface baffles were built in the effluent channels of the last two tailings ponds to retain the scum or film present on the surface of the ponds.

Studies and analyses performed in the laboratory involved the evaluation of the physical and chemical characteristics of the waste water samples. Sodium isopropyl xanthate concentration was determined by means of potentiometric titration and microscopic studies were made of the algal growths causing problems in the receiving stream. Algal growth studies were conducted to determine the nutrient properties of waste water from the flotation process and the measurement of lead, zinc, and copper concentration in the algal mats.

A. Characterization of Mining and Milling Waste Waters

1. Dissolved Oxygen

The dissolved oxygen (DO) content of the waste water was determined so that the amount of oxygen available for

microbial decomposition of the flotation process waters would be known. The DO determinations were made using the Winkler Azide Method as described in Standard Methods (24). Dissolved oxygen was determined for water samples from: the lead, zinc, and copper thickener effluents; the tailings effluent; the septic tank effluent; and each of the three tailings ponds.

2. Biochemical Oxygen Demand

The biochemical oxygen demand (BOD) determinations of the waste water samples were made to find out how much dissolved oxygen would be required for microorganisms to aerobically decompose the flotation process waste. The BOD of the waste water samples was measured using 300 ml BOD bottles as recommended by Standard Methods (24). The five day BOD was determined for water samples from: the lead, zinc, and copper thickener effluents; the sanitary septic tank effluent; and each of the three tailings ponds. The samples were diluted to various concentrations so that one or more dilutions would produce a depletion of at least 2 mg/l and have at least 0.5 mg/l of dissolved oxygen remaining at the end of the incubation period (25). Since some of the flotation reagents that are present in the waste water are known to break down in seven days, ten day BOD tests on samples from the lead, zinc, and copper thickener effluents, the tailings effluent, and the three

tailings ponds were run to see if the additional incubation time would cause any material difference from the results obtained with the standard five day BOD test.

3. Chemical Oxygen Demand

Chemical oxygen demand (COD) determinations were made so that the total amount of oxidizable material present in the flotation process waste would be known. The COD determinations were made using 20 ml samples according to techniques outlined in Standard Methods (24). The COD was determined for samples from the lead, zinc, and copper thickener effluents and the tailings effluent.

4. Solids Determination

The solids contents of the waste waters were determined by gravimetric analysis according to Standard Methods (24). Porcelain evaporating dishes and gooch crucibles with fiberglass filter mats were used for the analysis. Weights of the solids were measured with a Sartorius Analytical Balance*. The total, fixed, volatile, total suspended, fixed suspended, and volatile suspended solids were determined for samples from the combined lead and zinc thickener effluents and each of the three tailings ponds. The tailings effluent was not analyzed since it contained large amounts of crushed dolomite.

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*A Product of Brinkman Instruments, Inc., New York, N. Y.

5. Phosphorus

The phosphorus concentrations of the waste waters were determined because phosphorus is one of the major nutrient elements required for normal growth of algae (26). The phosphorus concentrations were determined by the analytical procedure reported by Jankovic, Mitchell, and Buzzell (27). Sulfuric acid and potassium persulfate were added to a 10 ml sample and the mixture boiled for 15 minutes. After cooling, the sample was diluted fifty times and a mixed reagent containing sulfuric acid, molybdate solution, ascorbic acid solution, and tartrate solution was added. After allowing 10 minutes for color development, the samples were observed for absorption at a wavelength of 710 mμ using a Model 139 UV-VIS Perkin - Elmer Spectrophotometer*. The phosphorus concentration was determined by comparing the absorption of the sample with that of a calibration curve prepared using standard phosphate solutions. The phosphorus concentration was carried out for each of the three tailings ponds and for Stations 6, 7, and 8 in Bee Fork Creek.

6. Nitrogen

The nitrogen concentrations of the waste waters were determined because nitrogen is required for normal algal growth (26). The nitrogen concentrations were determined by the total Kjeldahl nitrogen method as described in

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*A Product of Hitachi, Ltd., Tokyo, Japan

Standard Methods (24). The nitrogen concentration was determined for water samples from each of the three tailings ponds.

7. Fluoride

Fluoride concentrations of the waste waters were determined because drinking water containing excessive fluorides can cause bone changes in humans and animals alike (28). The fluoride concentrations were determined by the SPANS method described in Standard Methods (24). A Delta Water Analyzer Model 260* was used as the photometer. The reagents and processes employed were in accordance with the manufacturer's specifications. The fluoride concentrations were determined for each of the three tailings ponds and the sampling Stations 6, 7, and 8 on Bee Fork Creek.

8. Hydrogen Ion Concentration (pH)

The pH of the waste waters was determined to be certain that water was not acidic. If the waste water becomes acidic, the heavy metals contained in the flotation process waste will not be precipitated in the tailings ponds, but will remain in solution and flow into Bee Fork Creek. Measurements of pH were performed with a Beckman Zeromatic pH Meter** with manual temperature control. This

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*A Product of Delta Scientific Corp., Lindenhurst, L. I., N. Y.
**A Product of Beckman Instruments, Inc., Fullerton, Calf.

instrument was calibrated each time before use with a buffer solution having a pH of 6.8 at 25° C. The pH was determined for samples from all of the tailings ponds and Stations 6, 7, and 8 on Bee Fork Creek.

B. Potentiometric Titration of Sodium Isopropyl Xanthate

The evaluation of a flotation process waste treatment method would be enhanced by a good method of flotation reagent analysis. The potentiometric titration method was chosen from all the methods of reagent analysis reviewed in the literature survey (Chapter III) because of its seemingly relative simplicity and the availability of necessary equipment. The analysis of sodium isopropyl xanthate was carried out by titrating a purified xanthate solution with silver nitrate ($AgNO_3$) solution according to Du Rietz (16).

The sodium isopropyl xanthate was purified by dissolving a commercial grade sample in ethyl alcohol, filtering off the insoluble residue, and precipitating with diethyl ether. The precipitate was then retreated by the same procedure and the purified xanthate obtained was washed with ether (15).

The titration was performed by adding silver nitrate solution, drop by drop, into the xanthate solution and measuring the potential of a silver electrode immersed in the xanthate solution against that of a standard calomel electrode. The calomel electrode could not come in

direct contact with the xanthate solution being titrated. The potassium chloride (KCl) which leaks from the calomel electrode would react with the silver nitrate to form silver chloride (AgCl) and thus, produce erroneous results. For this reason, the calomel electrode was immersed in a saturated potassium nitrate (KNO_3) solution connected to the xanthate solution being titrated by a salt bridge made of a glass "U" tube filled with potassium nitrate and a gelatin mixture. The salt bridge allowed current to flow from one solution to the other but prevented chloride ions from reaching the xanthate solution. The potentials were measured on the millivolt scale of a Beckman Zeromatic pH Meter* and recorded as the silver nitrate was added to the xanthate solution. The xanthate solution was agitated with a magnetic stirrer. Various concentrations of silver nitrate solution and xanthate solution were used in different titrations to determine the reproducibility of the analysis.

C. Microscopic Examination of Undesirable Algal Growths From the Field

A microscopic study of the undesirable filamentous algal growths was undertaken to determine if algal changes had taken place since the study by Handler in 1968 (5). The microscopic study was conducted by observing field

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*A Product of Beckman Instruments, Inc., Fullerton, Calf.

samples of the algal growths under a Bausch and Lomb Model PB-252 Dynazoom Microscope*. Microphotographs of selected specimens were taken using a $3\frac{1}{4}$ x $4\frac{1}{4}$ inch Polaroid Camera Attachment** or a Kodak 35 millimeter Camera Attachment***.

D. Studies of Algal Growth in Flotation Process Waste

Algal growth studies were conducted to determine the nutrient properties of the flotation process waste water. Algal growth studies were conducted in the laboratory under controlled conditions and outside the laboratory under natural environmental conditions. In both studies, field samples of algal mats from Tailings Pond III were used after being fed with a nutrient solution made up of glucose, phosphate, and nitrate salts. The filamentous algae were rolled out flat and plugs, one inch in diameter, were cut from the samples. Also, small samples of algae were removed from the plugs, placed on a microscope slide, and photographed. The algal plugs were weighed and then placed in growth chambers filled with demineralized water. The algal plugs were placed on aluminum wire screens which were suspended by wire from the tops of the chambers. This prevented the algal plugs from settling to the bottom of the growth chambers which would have prevented them from

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*A Product of Bausch and Lomb, Rochester, N. Y.
**A Product of Polaroid Corp., Cambridge, Mass.
***A Product of Kodak Corp., Rochester, N. Y.

receiving light. In both studies, a feed made up of equal volumes of waste water from the lead and zinc thickener effluents and the tailings effluent was added daily to the growth chambers. The amounts of waste added per day to the growth chambers corresponded to 0.5, 1, and 5 percent of the volumes of water in the growth chambers. The daily flow of flotation process waste water is approximately one percent of the volume of Tailings Pond III.

The algal growth studies were started on July 3, 1969 and continued for 20 days. At the end of this time, the algal plugs were retrieved from the growth chambers and dried of excess water. The diameter of the algal plugs was measured and their weights were then determined. Small samples of algae were removed from the plugs, placed on a microscope slide, photographed, and compared with the photographs taken of the same algal plugs at the start of the study to observe if changes had taken place in the condition of the algal cells.

1. <u>The Outside Growth Chambers</u>

The three growth chambers used for the outside algal growth study were one-gallon wide-mouthed jars with the tops removed. The growth chambers were filled with two liters of demineralized water and placed on a bench located on the roof of the Civil Engineering Building at the University of Missouri-Rolla. This position gave the

growth chambers a southern exposure and the experimental set up was accessible through a window in the Sanitary Engineering Laboratory. Outside growth chambers were subjected to the natural weather conditions during the month of July. The algal plugs were placed in the growth chambers as described above.

2. The Laboratory Growth Chambers

The three growth chambers used for the laboratory algal growth study were improvised from nine pound sulfuric acid bottles with the bottoms removed by a special sawing process. The bottomless bottles were inverted and a two-hole cork was inserted into each of the bottle necks. An air line was passed through one hole and a drain line was placed through the other. These assemblies were held in place by ringstands and clamps and then placed in a plantarium (environmental chamber) (Figure 17). The temperature in the plantarium was maintained between 80 and 85° F and the humidity adjusted through the use of a water saturated sponge wick. Radiant energy needed for algal photosythesis was provided by two G. E. "Plant Life"* fluorescent lamps which were controlled by automatic timers to give a twelve-hour photoperiod and a twelve-hour dark period. Air was bubbled through an airstone diffuser into the growth

*A Product of the General Electric Corporation

Figure 17. Laboratory Growth Chambers Inside the Plantarium.

chambers to assure that the algal plugs received sufficient carbon dioxide to promote growth. The air source used was a compressed air spigot at the laboratory bench in the Sanitary Engineering Laboratories. A water trap was placed in the air line to trap oil droplets from the compressed air and to increase the humidity of the air so that water evaporation in the growth chambers could be reduced. An activated carbon filter was also placed in the air line to remove any material that may have passed through the water trap. The air flow was controlled by a pinch clamp on the air line connected to each growth chamber. The algal plugs were placed in the growth chambers as previously described.

E. Measurement of Heavy Metals in the Undesirable Algal Growths

The concentration of heavy metals contained in the filamentous algal mats could be harmful to aquatic life. The concentration of lead, zinc, and copper contained in algal samples from the field was determined with atomic absorption spectroscopy (29). The instrument used to make the analysis was Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer* belonging to the Geology Department of the University of Missouri-Rolla. Before analysis, one series of algal samples was cleaned of mud and dolomite

*A Product of Hitachi, Ltd., Tokyo, Japan

flour by shaking and washing the algal mats in a cylinder and decanting off the dirty water. The procedure was repeated until the wash water was relatively clean. The cleaned algal mat was then dried overnight in an oven at 110° C and the dried algae was pulverized. Approximately two and one-half grams of the pulverized algae were ashed in a muffle furnace at 600° C for two to three hours. After cooling, the weight of ashed algae was recorded and the ash dissolved in 25 milliliters of a mixture of one part concentrated hydrochloric acid, one part concentrated nitric acid, and eight parts deionized water. The solution was heated to boiling for a few minutes to assure complete solution of the ash. The solution was then filtered through a No. 42 Whatman filter paper into a 50 ml volumetric flask and the excess volume in the flask was made up with demineralized water. This solution was aspirated directly into the flame of the atomic absorption spectrophotometer for analysis (30).

An alternate method employing hydrogen peroxide extraction was used to separate the organic fraction of the algal mat from the inorganic dolomite flour which was trapped in the slime associated with the algae. This method consisted of dissolving two and one-half grams of dried algae in 75 milliliters of 10 percent hydrogen peroxide solution over a time period of four hours to oxidize the organic fraction of the sample. This solution

was filtered through No. 42 Whatman filter paper and the filtrate was collected in a 100 ml volumetric flask. The excess volume of the flask was made up with demineralized water. This filtrate was aspirated directly into the atomic absorption spectrophotometer flame. The residue left on the filter was washed from the filter with demineralized water, collected, dried, and dissolved in a solution of one part hydrochloric acid, one part nitric acid, and eight parts demineralized water. This solution was also filtered through No. 42 Whatman filter paper into a 50 ml volumetric flask, the remaining volume being made up with demineralized water. This sample was aspirated directly into the atomic absorption spectrophotometer flame (30). Algal samples from Tailings Ponds II and III and bottom samples from Ponds I, II, and III were analyzed for lead, zinc, and copper content. Samples of the green algae, Spirogyra, taken from the West Fork-Black River at the low water bridge on Reynolds County Highway KK were also analyzed. These samples were analyzed to determine the heavy metal concentrations of algae growing in water not polluted by mining waste. Reagent blanks were prepared with only the acid solution and the hydrogen peroxide solution.

F. Field Studies

1. Sampling

All water samples were collected in the field in one-liter polyethylene plastic bottles with screw on caps. These bottles had previously been cleaned with chromic acid cleaning solution (24) and rinsed several times with tap water in the laboratory and rinsed twice in the field with the water being sampled.

All water samples were taken in such a manner as to collect a representative sample. Water samples were collected from the mill processes effluents by putting the mouth of the bottle directly into the effluent stream.

All samples were returned to the laboratory and stored in a walk-in refrigerator maintained at a temperature of 10^{o} C until analysis could be made.

2. Observation

Observation at the tailings ponds and Bee Fork Creek consisted of looking for signs of visible mining waste pollution such as color, scum, unusually heavy algal blooms, and buildups of dolomite flour. The observation also included odor perception of the water to determine if any trace of the unique flotation reagent smell was present.

3. Surface Baffle Experiment

At the author's request, surface baffles were constructed by the St. Joseph Lead Company at Fletcher Mine in the effluent channels of Tailings Ponds II and III

(Figure 3). A baffle was not constructed at Pond I because the tailings effluent is discharged into the second pond. The purpose of the surface baffles was to prevent the outflow of scum and film that had been observed floating on the surface of the tailings ponds. It was suspected that this scum and film consisted of waste flotation reagents including sodium isopropyl xanthate and frother alcohols. It was believed that the breakdown of these organic compounds was at least partly responsible for the excessive blue-green algal growths. As shown in Figure 18, sodium isopropyl xanthate was found to support bacterial growth. Wixson (31) reported that other alcohol compounds also increase bacterial growth. Prolific bacterial growths produce carbon dioxide as a waste product of oxidation. This carbon dioxide will enhance the growth of the blue-green algae which will produce oxygen as a by-product of photo-synthesis and in turn enhance the growth of bacteria. This mutual symbiotic relationship between bacteria and blue-green algae is discussed in great detail by Kuentzel (32).

The baffles were constructed of 2" x 12" timber planks which spanned the entire width of the effluent channel. The planks were supported by 4" half-posts placed at the plank connections and as needed for extra support (Figures 19 and 20).

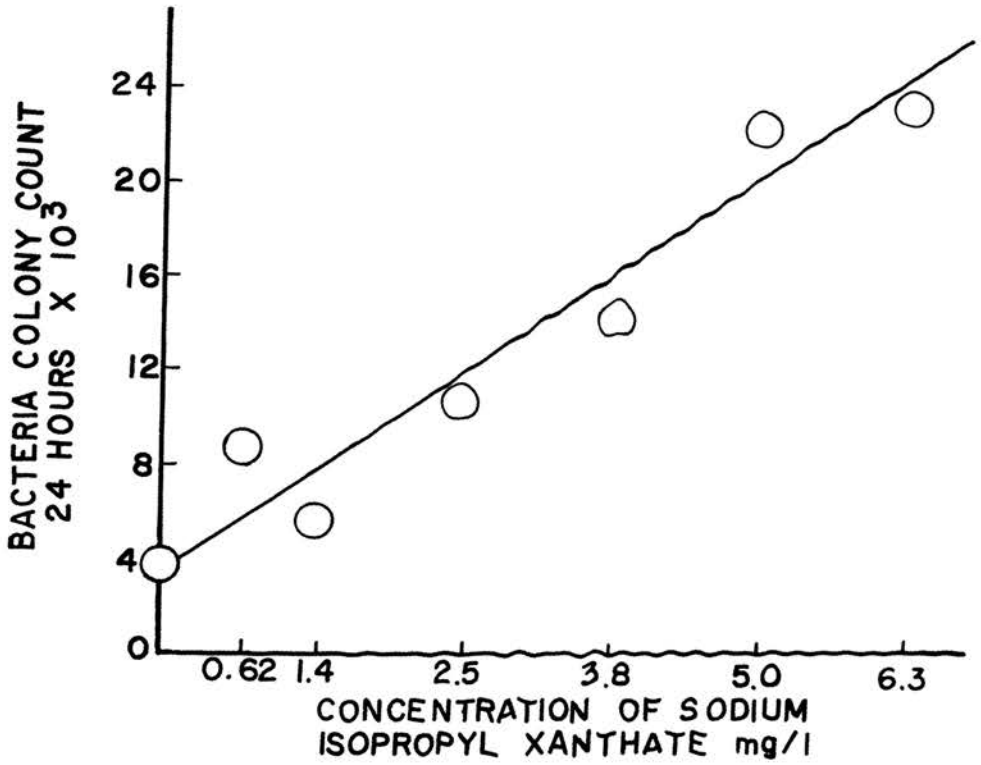

Figure 18. Growth of Bacteria Using Sodium Isopropyl Xanthate as Food Source (4).

Figure 19. Plank Baffle in the Effluent Channel of Tailings Pond II.

Figure 20. Plank Baffle in the Effluent Channel of Tailings Pond III.

The surface baffle at Tailings Pond II was built in water which was too shallow and the water flow under the baffle was found to be too rapid and turbulent to retard the surface film. A hanging baffle was then constructed from a long canvas air pipe which was split and hung over a cable which was supported by sets of floating 55 gallon oil drums (Figure 21). The hanging baffle was placed in the deeper water of the effluent channel, just upstream of the plank baffle as shown at the left-side of Figure 19.

Figure 21. Hanging Baffle Supported by a Cable and Oil Drums Just Outside the Entrance to Effluent Channel of Tailings Pond II.

V. RESULTS

A. Characterization of Mining and Milling Waste Waters

The results of the characterization of the mining and milling waste waters are presented in Tables III, IV, and V. Because a characterization of the waste had been reported by Handler (5), the data reported was the result of one anlysis unless otherwise noted.

B. Potentiometric Titration of Sodium Isopropyl Xanthate

The potentiometric titration of sodium isopropyl xanthate did not produce results in accordance with those published by Du Rietz (16). Even though the instructions presented by Du Rietz were followed as closely as possible, the potential between the electrodes in the xanthate solution produced a meter reading of +510 to +630 millivolts instead of -460 millivolts as reported. As the silver nitrate was added, the potential of the xanthate solution became more positive which was in agreement with Du Rietz's results, but, the meter soon went off scale making analysis impossible. It was then decided to set the meter for full scale deflection and manually set the meter reading to 0 millivolts at the start of the titration of a 10 milligram per liter xanthate solution to see if a proportional relationship could be established between the concentration of xanthate solution and the volume of silver nitrate titrated at a certain meter

TABLE III

Analysis of Dissolved Oxygen, 5-Day Biochemical Oxygen Demand, 10-Day Biochemical Oxygen Demand and Chemical Oxygen Demand

Sample	Dissolved Oxygen mg/l O_2*	5-Day BOD mg/l O_2	10-Day BOD mg/l O_2	Chemical Oxygen mg/l O_2**
Lead, Zinc, & Copper Thickener Effluent	0.0	59	50	170
Tailings Effluent	0.0	--	13	50
Tailings Pond I	8.8	3	5	--
Tailings Pond II	9.6	2	4	--
Tailings Pond III	9.6	2	3	--
Septic Tank Effluent	0.0	112	--	--

*Samples collected on February 13, 1969.
**Average of two analyses.

TABLE IV

Analysis of Phosphorus, Nitrogen, and Fluoride

Sample	Phosphorus, mg/l P*	Nitrogen, mg/l N	Fluoride, mg/l F**	pH Units**
Tailings Pond I	<0.1	<1.0	1.6	7.9
Tailings Pond II	<0.1	<1.0	1.5	8.2
Tailings Pond III	<0.1	<1.0	1.4	8.1
Station 6	<0.1	- -	0.1	7.7
Station 7	<0.1	- -	1.4	8.4
Station 8	<0.1	- -	1.3	8.3

*Results of two analyses.
**Average of three analyses.

TABLE V

Solids Determination

Determination	Lead & Zinc Thickener	Tailings Pond I	Tailings Pond II	Tailings Pond III
Total Solids, mg/l	964	504	484	436
Fixed Solids, mg/l	84	130	64	58
Volatile Solids, mg/l	880	374	420	378
Total Suspended Solids, mg/l	148	12	7	4
Fixed Suspended Solids, mg/l	0	0	0	0
Volatile Suspended Solids, mg/l	148	12	7	4

reading. This procedure produced titration curves as shown in Figure 22. These curves indicated a good proportional relationship between xanthate solutions of 1, 5, and 10 milligrams per liter at a meter reading of one hundred. It was found, however, that these results could not be reproduced. The results of the subsequent titrations did not agree with those of the previous titrations and were varied considerably by even a slight change of the rate of titration. Because of the complexity of these difficulties and lack of definitive results, this phase of the research was terminated.

C. Microscopic Study of the Undesirable Algal Growths From the Field

The microscopic study of the algal growths causing problems indicated that the algal mats consisted mainly of the blue-green algae, Oscillatoria (33) (Figure 23). Combined with the blue-green algae were other algae, bacterial growths, protozoa, rotifers, and neamatodes. Also, a large amount of rock flour from the tailings were enmeshed in the slime of the older algal mats (Figure 24).

D. Studies of Algal Growth in Flotation Process Waste

The results of the algal growth studies are presented in Table VI. The algal plugs failed to grow significantly during the test period. As shown in Table VI, one-half of the plugs broke up before the test was completed. Photomicrographs of samples from the algal plugs are shown in

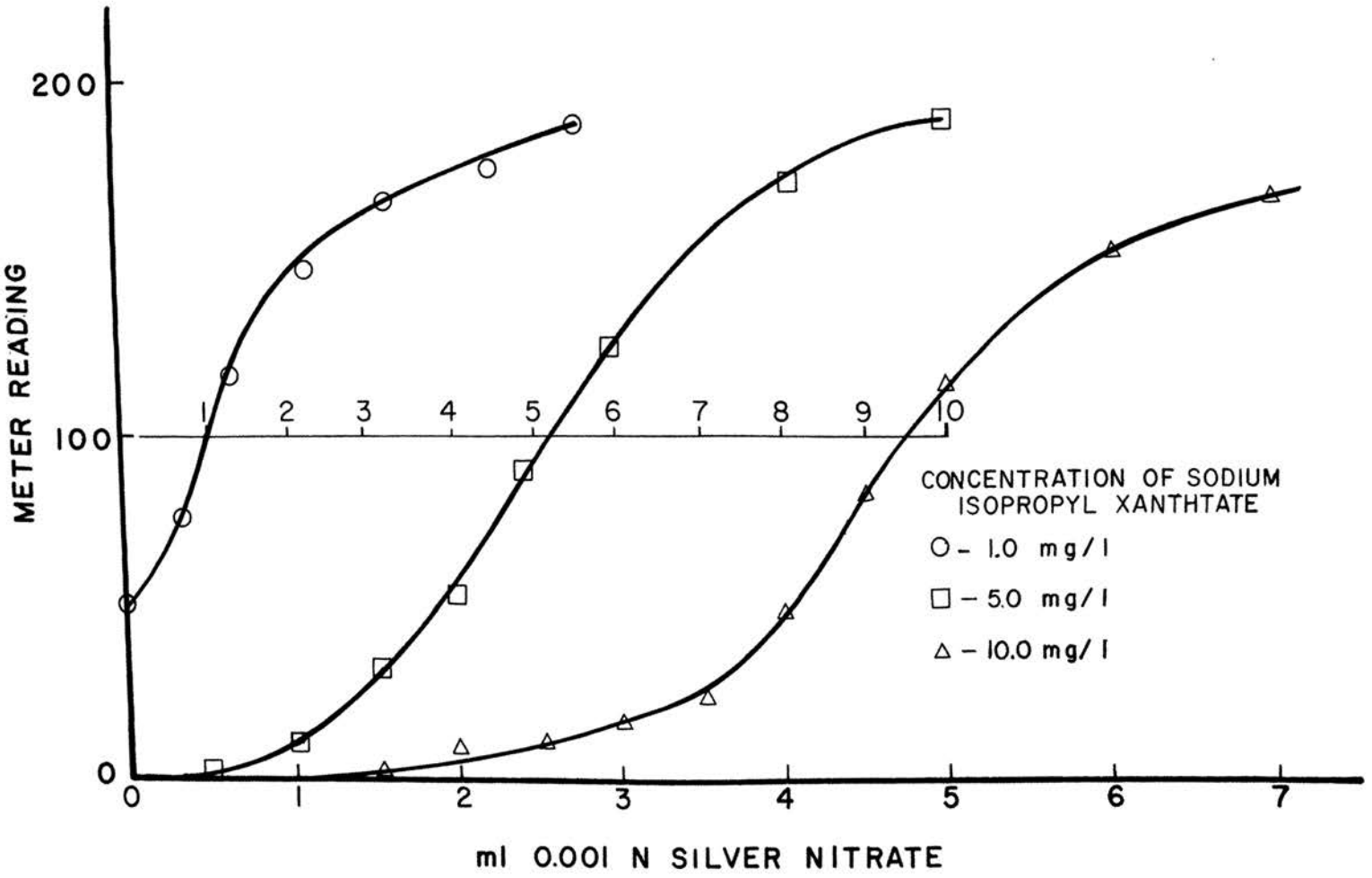

Figure 22. Titration Curves for Sodium Isopropyl Xanthate Solutions of 1, 5, and 10 mg/l with 0.001 N Silver Nitrate. Note the Proportional Relationship of the Curves at a Meter Reading of 100.

Figure 23. Photomicrograph of the Blue-Green Algae, Oscillatoria, Contained in the Algal Growths Causing Problems. 400 x

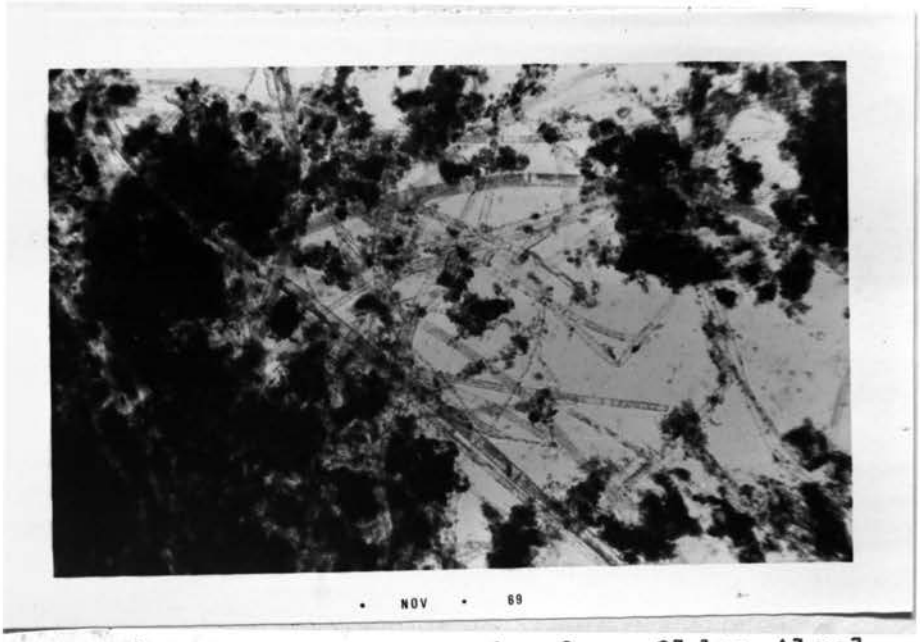

Figure 24. Photomicrograph of an Older Algal Mat Showing the Rock Flour Enmeshed in the Algal Slime. 200 x

TABLE VI

Algal Growth Studies

Growth Studies	Waste Feed ml/Day	Start of Study July 3, 1969		End of Study July 23, 1969	
		Plug Dia., Inches	Plug Weight, Grams	Plug Dia., Inches	Plug Weight, Grams
Outside Algal Growth Study, 2 Liter Growth Chambers	10	1.0	1.1	Broke Up	1.6
	20	1.0	1.1	Broke Up	1.6
	100	1.0	1.0	1.0	2.2
Laboratory Algal Growth Study, in 1.5 Liter Growth Chambers	7.5	1.0	0.9	1.0	1.3
	15	1.0	1.3	1.1	1.5
	75	1.0	1.4	Broke Up	1.7

Figures 25 and 26. As shown in Figure 25, before the study was started, the algal plugs consisted mainly of Oscillatoria, Scenedesmus, and Euglena. After the study was completed, the algal plugs seemed to consist almost entirely of old age filaments of Oscillatoria with Chlorella as shown in Figure 26. The algal plugs became completely covered with rock flour from the tailings contained in the feed waste.

E. Measurement of Heavy Metals in Algal Growths

The results of the atomic absorption spectroscopy of the ashed algal samples and tailings ponds' bottom samples dissolved in acid are shown in Table VII. The concentrations of lead, zinc, and copper contained in the algal mats and bottom samples are presented as micrograms (ug) of metal per gram of sample ash and are the results of one analysis. In all cases, lead is the predominant metal as expected, but, the unexpected results were the high concentrations of metals in the samples from the West Fork-Black River, an unpolluted stream.

The alternate method employing the hydrogen peroxide extraction to separate the organic fraction of the algal mats from the inorganic dolomite flour was unsuccessful. The hydrogen peroxide extract of the organic algal tissue failed to extract metals that may have been contained in them. The filter residues from the hydrogen

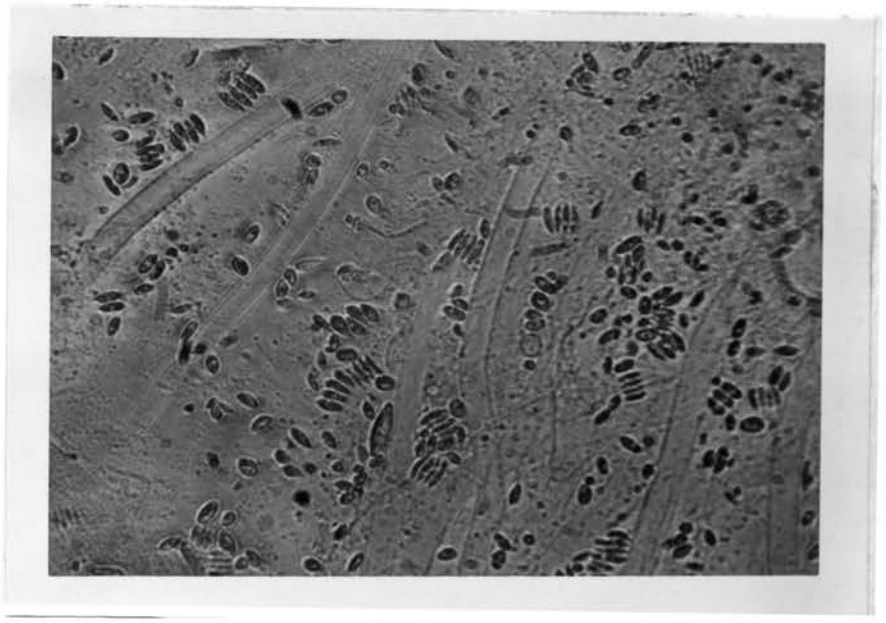

Figure 25. Photomicrograph of an Algal Plug at the Start of the Growth Studies. 400 x

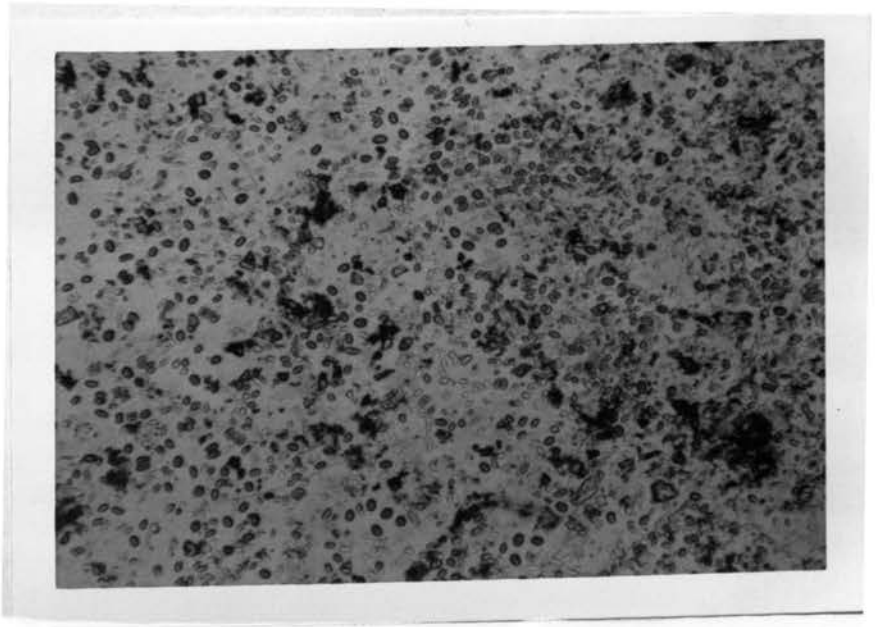

Figure 26. Photomicrograph of an Algal Plug After the Growth Study Period. 200 x

TABLE VII

Measurement of Heavy Metals in Algal Mats and Tailings Pond Bottom Samples

Unwashed Algal Samples	Ashed Sample Weight, Grams	Concentration of Metal, µg Metal/g Ash Sample		
		Lead	Zinc	Copper
Tailings Pond II	2.27	2,780	250	290
Tailings Pond III	2.00	2,000	270	200
West Fork-Black River	1.61	7,800	850	310
Washed Algal Samples				
Tailings Pond II	2.19	930	250	360
Tailings Pond III	2.11	1,420	260	170
West Fork-Black River	0.62	13,180*	2,400*	750*
Tailings Pond Bottom Samples				
Tailings Pond I	2.28	240	525	260
Tailings Pond II	2.40	710	960	250
Tailings Pond III	2.29	720	250	280

*Accuracy of these values are in doubt due to the small ashed sample weight.

peroxide extractions yielded heavy metal concentrations similar to those presented in Table VII.

F. Surface Baffle Experiment

The surface baffle experiment appeared to be very successful. The baffles retained and built up the surface scum and film that had previously flowed out of the tailings ponds and into Bee Fork Creek. The hanging baffle in the effluent channel of Tailings Pond II backed up enough scum and surface film to cover most of the pond's surface area as shown in Figure 27. Even though poor hydraulic conditions existed, the plank baffle in the same effluent channel retained a small amount of scum that washed under the hanging baffle (Figure 28). As shown in Figures 29 and 30, the plank baffle in the effluent channel of Tailings Pond III retained and backed up a much thicker and dirtier scum than that of Pond II.

The scum and surface film would continuously back up behind the baffles until washed away by rain fall. After periods of rain, the scum and surface film would be gone completely for a few days (Figure 31).

The mat-like algal growths that had previously been causing problems in Bee Fork Creek were growing in the area of the baffles in Tailings Ponds II and III (Figure 32). Although the creek was free of great masses of algal growths, the creek bottom was still covered by a

Figure 27. Tailings Pond II, Showing the Scum and Surface Film Backed Up by the Hanging Baffle in the Background.

Figure 28. Scum and Surface Film Behind Plank Baffle in the Effluent Channel of Tailings Pond II.

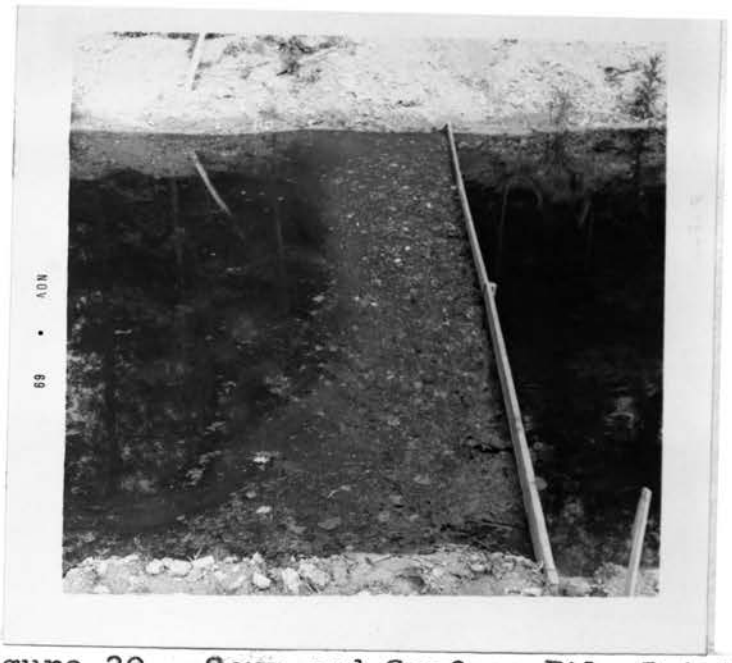

Figure 29. Scum and Surface Film Retained Behind the Plank Baffle in the Effluent Channel of Tailings Pond III.

Figure 30. Close-Up of Scum Behind the Baffle in Pond III. Note the Algal Growths on the Channel Bottom.

Figure 31. The Author Inspecting Baffles in Tailings Pond II After Rain had Washed Away the Surface Film.

Figure 32. Algal Growths Near the Baffles at Tailings Pond II.

thin layer of slimy rock flour as can be seen in Figure 33 and the unique odor of flotation reagents could also be detected.

Figure 33. Bee Fork Creek, Station 7 Showing Improved Stream Bottom as Compared to Stream Bottom Shown in Figure 2.

VI. DISCUSSION

The results of the characterization of the mining and milling waste waters indicate that all of the undesirable properties of these wastes cannot be detected by standard procedures of waste water analysis. The normal parameters of BOD, nitrogen, and phosphorus concentrations were very low for the tailings ponds, yet, prolific algal growths existed in these ponds. The growth of the blue-green algae, Oscillatoria, may have been stimulated by an unknown nutrient or trace metal. The fact that the COD levels were much greater than the BOD values indicated either that the waste flotation reagents are not completely biodegradable, or that materials toxic to microorganisms are present. The only two parameters which indicate significant pollution are the fluoride concentration and the volatile solids concentration. The fluoride concentration of the waste is naturally reduced to a safe level before discharge into Bee Fork Creek. The failure of the potentiometric titration of sodium isopropyl xanthate to repeat the results of previous experiments may probably be blamed upon natural deterioration of the xanthate solution used. After this titration procedure had been abandoned, Chen (34) discovered that the xanthate solution with which he was working deteriorated rapidly when stored at room

temperature. The titration procedure would produce more constant results if fresh xanthate solutions were made up before each titration. The algal growths causing problems consisted mainly of the blue-green algae, Oscillatoria, and had not changed materially since Handler's report (5).

The failure of the algal plugs to grow during the algal growth studies can be attributed to several circumstances. The waste added to the growth chambers contained tailings in suspension which completely coated the algal plugs each time the waste was added. This coating greatly reduced the amount of light available to the algae. Also, the changes of environment before and during the growth studies may have been too rapid to allow the algae time to adapt.

The concentrations of heavy metals contained in the algal mats of Oscillatoria are sufficiently high to warrant concern. The fact that the soil samples from the bottom of the tailings ponds also have excessive heavy metals content and so much inorganic material is contained within the algal mats indicates that the algal mats may accumulate the heavy metals on the bottom of the tailings ponds. This, however, was not the case for the growth of Spirogyra in the West Fork-Black River. The bottom of the stream consists of clean gravel, thus, there was no soil to collect the heavy metals. It is the

author's belief that the algal growths in the tailings ponds should not be allowed to enter Bee Fork Creek as the heavy metals contained in the mats may be harmful to aquatic and other animal life.

The surface baffle experiment indicates that many of the undesirable pollutional effects of the flotation process waste water can be eliminated by preventing the scum and surface film on the tailings ponds from reaching the receiving waters. Sufficient hydraulic detention time of the waste water in the tailings ponds is also necessary. Segregating the flotation process waste water from the relatively unpolluted shaft water would simplify the proper detention of the waste flotation reagents.

The observation that the surface baffles had eliminated the intense algal growths in the receiving stream points out an important fact. Nitrogen and phosphorus are not significant factors in the growth of the algal mats, because the baffles did not prevent these inorganic algal nutrients from reaching the stream. The baffles did, however, retain the scum and surface film. The intense algal growths then appeared in the area of the surface baffles. This indicates that the material contained in the scum and surface film is responsible for the intense algal growths.

VII. CONCLUSIONS

The following conclusions can be drawn from the results of this study:

1. Normal waste water parameters, such as BOD, nitrogen concentration, and phosphorus concentration, are not applicable to the evaluation of mining and milling waste waters at the Fletcher Mine in southeast Missouri.
2. Flotation process waste waters contain industrial reagents, some of which are present as scum and film floating on the surface of the tailings ponds.
3. The algal growths from the tailings ponds consisted of the filamentous, blue-green, Oscillatoria, and contained large amounts of rock flour enmeshed in the algal slime.
4. The filamentous algal growths from the West Fork-Black River and the algal mats from the tailings ponds contained considerable amounts of heavy metals.
5. The undesirable pollutional effects of the mining and milling waste water can be partially eliminated by preventing the discharge of the scum and film present on the tailings ponds' surface by surface baffles.

VIII. RECOMMENDATIONS FOR FUTURE STUDY

This study was made in conjunction with an overall research project for the New Lead Belt entitled, "Stream Pollution in the New Lead Belt of Southeast Missouri", and is based upon previous studies made by Handler (5) and Tibbs (29). A study of the toxic effects of flotation reagents was conducted by Chen (34) during the same time that this study was being conducted.

The results of this study indicate that the mining and milling waste waters contain substances which may be harmful to aquatic and animal life as well as material that is aesthetically objectionable. For this reason, more research must be carried out to determine the exact characteristics of mining and milling waste water and the toxic effects of all the materials contained in it. Practical methods of flotation reagent analysis need to be established so that reagent concentrations in the mill waste water can be determined.

The accumulation of heavy metals by filamentous algal growths needs to be studied further. The heavy metal concentrations in the West Fork-Black River should be investigated.

Finally, treatment methods which will more efficiently remove the objectionable waste reagents and dolomite flour from the mining and milling waste water need to be developed.

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VITA

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